Renewable and Sustainable Energy Reviews 18 (2013) 49–54

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Ozone depletion and global warming: Case for the use of natural refrigerant – a review

B.O. Bolaji [a,*], Z. Huan [b]

[a] Department of Mechanical Engineering, College of Engineering, Federal University of Agriculture, PMB. 2240, Abeokuta, Nigeria
[b] Department of Mechanical Engineering, Faculty of Engineering and the Built Environment, Tshwane University of Technology, Pretoria, South Africa

ARTICLE INFO

Article history:
Received 20 December 2011
Received in revised form
1 October 2012
Accepted 8 October 2012
Available online 3 November 2012

Keywords:
Ozone depletion
Global warming
Halocarbon
Alternative
Natural refrigerants

ABSTRACT

This paper presents natural refrigerants as the ideal, environmentally friendly refrigerants and the ultimate solution to the problems of ozone depletion and global warming. HFC refrigerants are currently the leading replacement for CFC and HCFC refrigerants in refrigeration and air-conditioning systems. However, they are equally foreign to nature like CFCs and HCFCs, consequently, strong basis for the need to embrace the use of natural refrigerants as replacement for the halocarbon refrigerants was provided. This paper also analyses potentials of various natural refrigerants and their areas of application in refrigeration and air-conditioning systems. Natural refrigerants especially hydrocarbons and their mixtures are miscible with both mineral oil used in R12 and poly-ol-ester oils used in R134a systems. Also, with exception of ammonia, they are fully compatible with all materials traditionally used in refrigeration systems. Finally, this paper has revealed that natural refrigerants are the most suitable long time alternatives in refrigeration and air-conditioning systems.

Contents

1. Introduction

Refrigeration technology plays an important role in modern life. It provides not only comfortable and healthy living environments but also regarded as necessities for surviving severe weather and preserving food. Especially, the preservation of food is vital to the stability and economic growth over the world. Conservation of food is achieved by slowing down biochemical processes to reduce the propagation of bacteria. This easily can be done by cooling or freezing and without extra preservatives.

Refrigeration technology gives the technical aids to cool food following the cold chain starting at production, transportation, finally storage, sale and storage at the consumer's home in a refrigerator without any interruption. Other uses include air-conditioning systems and industrial processes. Air-conditioning systems help to improve the comfort of human beings for private

* Corresponding author. Tel.: +23 48 185 791694; fax: +23 439243045.
E-mail addresses: bobbolaji2007@yahoo.com, bolajibo@funaab.edu.ng (B.O. Bolaji), HuanZ@tut.ac.za (Z. Huan).

1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2012.10.008

as well as for commercial purposes, to keep the health and increase the efficiency. However, accelerated technical development and economic growth throughout the world during the last century have produced severed environmental problems, forcing us to acknowledge that though these technological advances may contribute to human comfort, they also can threaten the environment through ozone depletion and global warming [1,2].

Ozone depletion and global warming are two major environmental concerns with serious implications for the future development of the refrigeration-based industries. The effects on the industry of the actions to reduce ozone depletion and global warming are now apparent. Ozone is a variant of oxygen, the ozone molecule having three atoms of oxygen. Ozone is a poisonous gas and if inhaled can cause death. Ozone layer surrounds the earth's stratosphere which is about 11 km above the earth surface. Life on the earth has been safe-guarded for thousands of years because of this life-protecting layer. It acts as shield to protect the earth against the harmful ultraviolet radiation from the sun [3].

Ozone layer efficiently screens all the harmful ultraviolet rays of the sun by absorbing most of the dangerous ultraviolet B (UV-B) radiation (Ultra-Violet A is allowed through while ultraviolet C is captured by oxygen). Since Ozone layer is a protector against harmful UV-B radiation, any damage to it could cause considerable harm to the environment and life on earth. Exposure to increased UV-B radiation can lead to incidents of eye damage (such as cataracts, deformation of eye lenses and presbyopia), cause skin cancer, reduce rates of plant growth, upset the balance of ecosystems, and accelerate the risk of disease [4].

Until the early 1970s nobody dreamt that human activity could threaten to deplete the ozone layer. Man is completely responsible for emissions of the most important ozone depleting and greenhouse gas halocarbons [4]. Halocarbons are a group of compounds which are mostly man-made gases consisting of both carbon and at least one of the halogens (fluorine, chlorine, iodine, and bromine). They are typically produced artificially for industrial purposes. They were first synthesised in 1928. Since then, they have come to be widely used for a variety of purposes such as propellants in aerosol cans, in the manufacture of soft and hard foams, in refrigeration and air conditioning, and as cleaning solvents [3]. The group includes chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydro-fluorocarbons (HFCs).

CFCs and HCFCs have been used for years as refrigerants, solvents and blowing agents. The stable structure of these chemical enables them to attack the ozone layer. If these chemical escapes into the atmosphere, they drift up to the stratosphere and intense UV-C radiation breaks their chemical bonds, releasing chlorine, which stripe an atom from the ozone molecule, reducing it to oxygen molecule. Chlorine acts as a catalyst, which accomplishes this destruction without itself undergoing any permanent changes; therefore it can go on repeating the process.

It has been discovered that one chlorine atom can destroy 100,000 ozone molecules. The higher the chlorine content of a compound, the longer will be its impact with the ozone layer. CFCs have more chlorine content than HCFC, therefore CFCs have higher potential for ozone depletion. The efficacy of ozone destruction is often measured by a comparative unit termed Ozone depletion potential (ODP), which is based upon the ODP of trichloro-fluoro-methane (CFC-11) being assigned a value of unity. It is estimated that CFCs contribute nearly 70% of man-made ozone depleting chemicals in the atmosphere [5]. The inventors of these refrigerants could not have visualised the ravaging effects of the refrigerants on the ozone layer. They intentionally pursued refrigerants with the exceptional stability that was imposed as one of the necessary requirements of the ideal refrigerant they were called upon to invent [6].

The second major environmental concern is climatic changes or global warming. This did not become a major area of attention until after the responses to ozone depletion had been initiated. Concerns on this issue are now beginning to complicate the handling of ozone depletion. In a green house, glass allows sunlight in but prevents some infrared radiation from escaping. The gasses in the earth's atmosphere, which exert a similar effect, are called "greenhouse gasses". Some of these greenhouse gasses include CFCs, HCFCs, CO_2, methane (CH_4) and nitrous oxide (N_2O). Different gasses absorb and trap varying amounts of infrared. They also persist in the atmosphere for different time period and also influence atmospheric chemistry in different ways.

Global warming arises because of the greenhouse effect. According to Ko et al. [7,8], the frequency distribution of the radiation coming from the sun closely approximates that from a black body at a temperature of about 5800 K, the spectrum wavelengths range from less than 1 nm to hundreds of metres, the peak in the spectrum is in the visible region at about 500 nm. When solar radiation ($1360\ \mathrm{W\,m^{-2}}$) arrives at the earth, about 30% is reflected back into space and most of the remainder passes through the atmosphere to the ground. This heats up the earth, which then behaves approximately as a black body, radiating energy with a spectral peak in the infrared. This infrared radiation cannot pass through the atmosphere because of absorption by water vapour, and other infrared absorbers. As a consequence, heat energy is trapped and the temperature at the surface of the earth is higher than it would be without the insulating blanket of the atmosphere.

Global warming is a good thing in itself and allows life to exist in all its variety [9]. The concern is that man's activities are increasing the concentration of greenhouse gases in the atmosphere, causing the amount of absorbed infrared radiation to increase, and leading to increased atmospheric temperatures and consequent long-term climate changes.

The amount of radiant energy that the refrigerants absorb is measured by an index called Global Warming Potential (GWP). GWP is the amount of infrared radiation that the gas can absorb, relative to carbon dioxide (with an assigned GWP of 1), integrated over a period of 100 years. A more appropriate measure of a refrigerant contribution to global warming is based on a concept called Total Equivalent Warming Impact (TEWI).

Hwang et al. [1] described two types of global warming effects. The first is the direct global-warming potential that is due to the emission of refrigerants and other pollutants. The second type is an indirect global-warming potential, which results from the emission of carbon dioxide due to the consumption of energy obtained from the combustion of fossil fuels (oil, natural gas, and coal). The combined effects of the two global warming potentials is known as TEWI.

The discovery of the two major environmental problems, discussed above, has resulted in a series of international treaties demanding a gradual phase out of halogenated fluids. The CFCs have been phased out in developed countries since 1996, and 2010 in developing countries. Initial alternative to CFCs included some hydro-chlorofluorocarbons (HCFCs), but they will also be phased out internationally by year 2020 and 2030 in developed and developing nations, respectively, because their ozone depletion potentials (ODPs) and global warming potentials (GWPs) are in relative high levels though less than those of CFCs [5,10,11].

Hydro-fluorocarbon (HFC) refrigerants have been found as the leading replacement for CFC and HCFC refrigerants in refrigeration and air-conditioning systems. However, international concern over relatively high global warming potential of HFC refrigerants has caused some European countries to abandon them as CFCs and HCFCs replacements. Hydrocarbons are the refrigerants favoured in many European countries [12]. It has

Table 1
Environmental effects of some common refrigerants.
Sources: [1,14,15].

Compositional group	Refrigerants	Ozone depletion potential (ODP)	Global warming potential (GWP) (100 years' horizon)
CFCs	R11	1	3800
	R12	1	8100
	R113	0.8	4800
	R114	1	9000
	R115	0.6	9000
HCFCs	R22	0.055	1500
	R123	0.02	90
	R124	0.022	470
	R141b	0.11	630
	R142b	0.065	2000
HFCs	R23	0	11700
	R32	0	650
	R125	0	2800
	R134a	0	1300
	R143a	0	3800
	R152a	0	140
Natural Refrigerants	R290	0	3
	R600a	0	3
	R717	0	0
	R718	0	0
	R744	0	1

already been suggested that HFC 134a may be decomposed by sunlight in the troposphere and form acid and poisonous substances [13]. If this should turn out to be true, the world may have to face yet another catastrophe, even worse than the CFC experience. HFCs are equally like CFCs and HCFCs foreign to nature, consequently, it is obvious and much preferable to use natural compounds, which are already circulating in quantity in the biosphere and are known to be harmless. The environmental effects of some common refrigerants are shown in Table 1. Therefore, in this review paper, the potentials of various natural refrigerants as long time alternatives in vapour compression refrigeration system are analysed.

2. Natural refrigerants

About 50 different substances have been more or less extensively used as working media over the 160 years of refrigeration history. Most of them have been discarded as unsuitable for various reasons, but a fair number of choice remains to adapt to varying conditions of application [16]. Among them are a number of natural refrigerants such as water, ammonia, hydrocarbons and carbon dioxide. Natural refrigerants provide alternatives to a number of CFC, HCFC and HFC refrigerants. In addition to their zero ozone depletion potential (ODP) and low or no global warming potential (GWP) (Table 1), they are compatible with common elastomer materials found in refrigerating systems and are soluble in conventional mineral oils. Since natural refrigerants contain no chlorine or fluorine atoms, they cannot undergo reaction with water and hence, do not form the corresponding strong acids that can lead to premature system failure. The potentials of some of these refrigerants as viable alternatives to ozone depleting refrigerants and greenhouse gases are analysed below:

2.1. Ammonia refrigerant

Ammonia has been a well-known refrigerant in large scale industrial applications for more than 120 years. The know-how concerning the technology is widely dispersed, in industrialised as well as in developing countries. Ammonia has excellent thermodynamic and transport properties, much superior to those of CFCs, HCFCs and HFCs. Ammonia plant always has considerably better energy efficiency in practice, when compressor speed, piping dimensions and heat transfer equipment are decided on the economic criteria [17]. Other important advantages are tolerance to normal mineral oils, low sensitivity to small amounts of water in the system, simple leak detection, unlimited availability and low price. All these factors contribute to its sustained popularity and wide application.

For large systems, the disadvantages of ammonia mainly concern safety; for small systems, there are presently additional cost disadvantages. The actual toxicity of ammonia is usually not a major concern; the smell is noticed by man at concentrations as small as 5 ppm. At the same time, the threshold limit value, which should not be exceeded for everyday exposure, is 50 ppm. Ammonia is unbearable for man at 500 ppm, while its acute toxicity starts at 2500 ppm and the flammability at 15 vol%. Obviously; nearly any hazard announces itself in far advance, making ammonia actually a very safe refrigerant concerning direct hazards [17].

However, there is an indirect hazard caused by use of ammonia in public areas: Heavy ammonia concentrations might cause (unnecessary) panic among those which are not familiar with the smell. The main focus of the safety measures is therefore to avoid a fast increase in ammonia concentration in public areas to or above the panic level.

Such, the safety rules for ammonia plants are very simple: No parts of a plant in direct contact with the public, and installation of systems to hold back significant ammonia amounts in case of a major rupture. While the former causes the need for indirect systems (which are per definition always present in case of water chillers), the latter leads to housings around the systems, often combined with a water tank. The water in such a tank allows solving a significant amount of ammonia completely. 50 l of water can solve 50 kg of ammonia. With such an amount, systems with up to 1.4 MW can be built [18].

2.2. Hydrocarbon refrigerants

Hydrocarbons (HCs) are the class of naturally-occurring substances that include propane, pentane and butane. HCs are excellent refrigerants in many ways – energy efficiency, critical point, solubility, transport and heat transfer properties. They are environmentally sound alternative for CFCs, HCFCs and HFCs. Hydrocarbons and their mixtures have zero ozone depletion potential and very low global warming potential (Table 2), they have no significant refrigeration related problems. The most important concern regarding the adoption of hydrocarbons as a refrigerant is their flammability. It should be remembered that millions of tonnes of hydrocarbons are used safely every year

Table 2
Environmental effects of some hydrocarbon refrigerants.
Sources: [19,20].

Data	Refrigerants		
	Propane (R290)	*n*-butane (R600)	iso-butane (R600a)
Natural	Yes	Yes	Yes
ODP	0.0	0.0	0.0
GWP, 100 years	3.0	3.0	3.0
Density at 25 °C (kg/m^3)	492.7	532.5	550.7
Flammability limits (vol%)	2.1–11.4	1.7–10.3	1.9–10.0
Molecular mass (kg/kmol)	44.1	58.1	58.1

throughout the world for cooking, heating, powering vehicles and as aerosol propellants. In these industries, procedures and standards have been developed and adopted to ensure the safe use of the product. It is essential that the same approach is followed by the refrigeration industry.

Hydrocarbons do not spontaneously combust in contact with air. Three elements need to coincide: (i) there must be a release of hydrocarbons, (ii) the hydrocarbon needs to mix with the correct proportion of air, the range of flammability being approximately between 1 and 10%, outside these limits combustion cannot occur, and (iii) an ignition source with energy greater than 2.5×10^{-4} kJ or a surface with a temperature exceeding 440 °C must be present. Any of the following measures must be taken to prevent potential fire or explosion:

(i) Contain the hydrocarbon either in a sealed system and/or reduce the number of connections.
(ii) Restrict the maximum charge of hydrocarbons.
(iii) Install ventilation such that the final concentration of hydrocarbons in air is below the lower flammability limit.
(iv) Eliminate the source of ignition associated with the system.

2.3. Water vapour refrigerant (R718)

Water has been looked at as refrigerant which is one of the ultimate natural refrigerants because of non-toxicity, non-flammability, zero-ODP, zero-GWP and very low cost. Water can be used as refrigerant in four ways: desiccant dehumidification/evaporative cooling, absorption chiller, adsorption chiller as well as compression chiller. The thermo-physical properties of water are consistent with a vapour compression chiller system that has the potential to achieve a high COP [21].

According to Lorentzen [18] open cycle water vapour systems are used occasionally for direct evaporation chilling in situations with low relative time of operation, when the high power consumption is of minor importance compared to investment and labour costs. The vapour volume to be compressed is enormous, in the same order of magnitude as for an open cold air cycle of similar capacity. Steam ejectors are normally applied.

Water has also been proposed as a refrigerant in regular systems using turbo- or special rotary compressors [22]. The physical dimensions of these machines become very large and price must be a problem. In the high temperature heat pump area on the other hand, water is an ideal working medium. It has been used extensively for many years in open systems for concentration of liquids by evaporation. Since the temperature lift is limited to what is required for heat transfer, the COP becomes very high, up to 20 or more in some cases. The low lift also permits the use of simple and relatively inexpensive single stage turbo compressors. For open or closed cycle heat pumps in a multitude of industrial applications in the temperature range of 80–100 °C water is the obvious choice [18].

2.4. Carbon dioxide refrigerant (R744)

Carbon dioxide (CO_2 or R744) is one of the few natural refrigerants, which is neither flammable nor toxic. It is inexpensive, widely available and does not affect the global environment as many other refrigerants. CO_2 has a GWP of 1, but the net global warming impact when used as a technical gas is 0, since the gas is a waste product from industrial production. CO_2 is an excellent alternative among the natural refrigerants, especially in applications where the toxicity and flammability of ammonia and hydrocarbons may be a problem. CO_2 has been regarded as favour across the broad spectrum of automotive, domestic, commercial and industrial refrigeration and air conditioning systems. The most important issues are to enhance the energy efficiency and reduce cost of the systems to an acceptable level [21].

R744 had been used as a refrigerant in the 1930 s and 1940 s in ships' refrigerator and other stationary systems. However, refrigerant capacity dropped rapidly when ships passed through tropical regions. R744 was abandon as a refrigerant because of lost capacity at higher ambient temperatures and the introduction of chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbon (HCFCs) [13].

R744 has the most favourable environmental parameters among all alternatives. It is non-flammable and non-toxic, and has very low GWP. Also important is the fact that it is not necessary to capture R744 refrigerant during the AC system refilling or reparation and at the end of life, which simplifies handling and introduces certain savings. Interest for using natural refrigerants especially R744 due to its favourable characteristics reappeared in late 1980s because of the increased awareness of environmental harmfulness of fluorocarbons.

The property that decisively defines behaviour of R744 in a refrigeration cycle is its low critical temperature (31.1 °C) [23]. Hence vapour compression cycle with R744 at ambient temperatures works usually partly above the critical point, and at much higher pressures than most halocarbon. Consequently, the process of heat rejection is not any more predominately condensation, but trans-critical vapour cooling with significant gaseous refrigerant temperature decrease inside the gas cooler (heat exchanger).

In order to improve the overall cooling performance and COP of the system, the refrigerant must be cooled in the gas cooler, which will bring the exit temperature as close as possible to the ambient temperature. In order to achieve highly efficient heat exchange in gas cooler multiport tube fin technology is used [24]. In general R744 heat exchangers offer more capacity than any halocarbon refrigerant of the same components' size and possess capacity for further improvement in terms of enhancement of air side heat transfer, becoming more package friendly (gas cooler) and condensed water vapour retention/drainage management (evaporator).

However, it is a possible disadvantage that the operating pressure of the transcritical refrigeration system using R744 is too high. One way to overcome this high pressure disadvantage may be a choice of cascade refrigeration system, where carbon dioxide refrigeration system is precooled by other refrigeration system [25,26].

3. Refrigerants and material compatibility

3.1. Lubricants

In vapour compression processes, the presence of oil is intrinsic and unavoidable since the oil is required to lubricate the internal moving parts for proper functioning of the compressor [27]. On the other hand, the lubricant provides a seal between the moving parts enabling efficient vapour compression [28,29]. Gibb et al. [30] had shown that the benefits of the introducing more energy efficient refrigeration lubricants can lead to a reduction in energy consumption as high as 15% and indirect reductions in emissions of the greenhouse gas CO_2. Despite its crucial role in increasing the energy efficiency of compressor, in typical operation of an air-conditioning or refrigeration system, a small amount of lubricant oil may migrate from the compressor and into another part of the system, such as the evaporator, condenser, expansion device, and connecting piping, thereby inevitably altering the heat transfer and frictional characteristics of the refrigerant [28,31].

Table 3
Selection guide for natural refrigerants.
Source: [16].

Sector	Compressor type	Refrigerant
Domestic fridge/ freezers	Sealed hermetic unit	R290, R600a,
Commercial equipment – medium temperature	Sealed hermetic unit	R290, R600a
	Accessible semi-hermetic	R290, R600a
	Reciprocating open drive	R290, R600a
Commercial equipment – low temperature	Sealed hermetic unit	R170, R290
	Accessible semi-hermetic	R170, R290
	Reciprocating open drive	R170, R290, R744
Large commercial and industrial	Reciprocating open drive	R170, R290, R600a, R717, R744
	Screw	R600a, R290, R744
Mobile air conditioning or refrigeration	Hermetic reciprocating open drive	R600a, R290
Air conditioning	Reciprocating open drive	R600a, R290, R717
	Centrifugal	R600a
	Accessible semi-hermetic	R290
	Screw	R600a, R717
	Hermetic	R600a

In order to minimise the negative effects on heat transfer and to ensure the oil return to the compressor the oil should be sufficiently miscible with the refrigerant. HFC refrigerants are not miscible with the mineral oils use in CFC systems. Therefore, synthetic ester-based oils and poly-alkylene-glycol-based oils are used with HFC refrigerants, which are significantly more expensive than mineral oils and very sensitive to humidity. Also, oil, water and HFC refrigerants may form acids in the refrigeration cycle, which can cause insufficient lubrication and thus damage the compressor. On the other hand, natural refrigerants especially hydrocarbons and their mixtures are miscible with both mineral oil used in CFC and poly-ol-ester oils used in HFC systems.

3.2. Metals and sealing materials

In refrigeration circuits a variety of different materials is used like steel, brass, copper and sealing materials. Some metals, especially alloys with zinc or solders with zinc show increased corrosion with ester based oils and HFC refrigerants. No problems of this kind are known for the use of hydrocarbons as refrigerant. Natural refrigerants, with exception of ammonia, are fully compatible with all materials traditionally used in refrigeration systems.

4. Selection guide for natural refrigerants

Refrigerants are selected so that they contribute to good system efficiency. Table 3 shows guide for possible selection of natural refrigerants for new equipment. The final application of alternative refrigerants is checked for compatibility with equipment and system design. Also, there is need for thorough investigation with both refrigerant suppliers and equipment manufacturers to ensure refrigerants are fully compatible with, and are suitable for, the application and system design.

5. Conclusion

Accelerated technical development and economic growth throughout the world during the last century have produced severed environmental problems, forcing us to acknowledge that though these technological advances may contribute to human comfort, they also can threaten the environment through ozone depletion and global warming. The halocarbon refrigerants used in the refrigeration and air-conditioning systems have become a subject of great concern for the last few decades. The problem is not with refrigerants inside the system, but with their release to the environment. Earth is the only planet in the solar system with an atmosphere that supports life; therefore, preserving the ozone layer and reducing the release of greenhouse gasses to the atmosphere are part of the many essential steps necessary for the protection of life on the planet for future generations.

CFCs and HCFCs were found harmful to the earth's protective ozone layer. Therefore, their production has been prohibited by the Montreal Protocol and other international agreements. HFC refrigerants are currently the leading replacement for CFC and HCFC refrigerants in refrigeration and air-conditioning systems. However, they are equally foreign to nature like CFCs and HCFCs, consequently, it is obvious and much preferable to use natural compounds, which are already circulating in quantity in the biosphere and are known to be harmless. Therefore, this paper discusses the problems and causes of ozone depletion and global warming. It provides strong basis for the need to embrace the use of natural refrigerants as replacement for the halocarbon refrigerants. It also analyses potentials of various natural refrigerants and their areas of application in refrigeration and air-conditioning systems. Natural refrigerants especially hydrocarbons and their mixtures are miscible with both mineral oil used in CFC and poly-ol-ester oils used in HFC systems. Also, with exception of ammonia, they are fully compatible with all materials traditionally used in refrigeration systems. Finally, this paper has revealed that natural refrigerants are the most suitable long time alternatives in refrigeration and air-conditioning systems.

References

[1] Hwang Y, Ohadi M, Radermacher R. Natural refrigerants. Mechanical Engineering, 120. Published by American Society of Mechanical Engineers (ASME); 1998 96–99.
[2] Bolaji BO. Selection of environment-friendly refrigerants and the current alternatives in vapour compression refrigeration systems. TRGJSM Journal of Science and Management 2011;1:22–6.
[3] Bhatti MSA. Historical look at chlorofluorocarbon refrigerants. ASHRAE Transactions Part 1 1999:1186–206.
[4] UNEP. United Nation environment program. Handbook for International treatics for protection of the ozone layers, 5th ed. Nairobi, Kenya, 2000.
[5] UNEP. United Nation environment program. Handbook for International treaties for protection of the ozone layers, 6th ed. Nairobi, Kenya, 2003.
[6] Cavallini A. Working fluids for mechanical refrigeration. International Journal of Refrigeration 1996;19:485–96.
[7] Ko MKW, Sze ND, Molnar G, Prather MJ. Global warning from chlorofluorocarbons and their alternatives: time scales of chemistry and climate. Atmospheric Environment 1993;27:581–7.
[8] Ko MKW, Sze ND, Prather M. Better protection of the ozone layer. Nature 1994;367:505–8.
[9] Segelstad TV. Carbon cycle Modelling and the residence time of natural and anthropogenic atmospheric CO_2: on the construction of the green house effect global warming dogma. Global Warming: the continuing debate. European Science and Environment Forum London 1998:185–218.

[10] Radermacher R, Kim K. Domestic refrigeration: recent development. International Journal of Refrigeration 1996;19:61–9.
[11] Bolaji BO. Performance investigation of ozone-friendly R404A and R507 refrigerants as alternatives to R22 in a window air-conditioner. Energy and Buildings 2011;43:3139–43.
[12] Boumaza M. Performances assessment of natural refrigerants as substitutes to CFC and HCFC in hot climate. International Journal of Thermal and Environmental Engineering 2010;1:125–30.
[13] Lorentzen G, Pettersen J. A new efficient and environmentally benign system for car air-conditioning. International Journal of Refrigeration 1993;16:4–12.
[14] Calm JM, Domanski PA. R22 replacement status. ASHRAE Journal 2004;46:29–39.
[15] Bitzer. Refrigerant Report. Bitzer International, 13th ed. 71065 Sindelfingen, Germany, 2007. 〈http://www.bitzer.de〉. (accessed 24.06.07).
[16] AIRAH. Air-conditioning and industry refrigerant: refrigeration selection guide. The Australian Institute of Refrigeration Air-conditioning and Heating (AIRAH), Australia, 2003.
[17] GTZ. Natural Refrigerants. Gesellschaft fur Technische Zusammenarbeit (GTZ) Yearbook, Germany, 1995.
[18] Lorentzen G. The use of natural refrigerants: a complete solution to the CFC/HCFC replacement. International Journal of Refrigeration 1995;18:190–7.
[19] Perry RH, Green DW. Perry's Chemical Engineers' Handbook. Section 2. 7th ed. New York, USA: McGraw-Hill; 1997.
[20] Fatouh M, El-Kafafy M. Assessment of propane/commercial butane mixtures as possible alternatives to R134a in domestic refrigerators. Energy Conversion and Management 2006;47:2644–58.
[21] Wang RZ, Li Y. Perspectives for natural working fluids in China. International Journal of Refrigeration 2007;30:568–81.
[22] Mads H, Minds G. Energy saving in process cooling by use of water as a refrigerant. International Journal of Refrigeration 1993;16:75–85.
[23] ASHRAE. Thermophysical properties of refrigerants. Atlanta (GA): ASHRAE Fundamental, Inc.; 2001 Chapter 20, p. 1–67.
[24] Antonijevic D. Technical and environmental aspects of synthetic refrigerants replacement by carbon dioxide in mobile air conditioning. Journal of Automobile Engineering 2004;218:1111–7.
[25] Robinson D, Groll E. Using carbon dioxide in a transcritical vapour compression refrigeration cycle. In: Proceedings of the sixth international refrigeration conference, Purdue university, July 1996, p. 25–28.
[26] Kim SG, Kim MS. Experiment and simulation on the performance of autocascade refrigeration system using carbon-dioxide as a refrigerant. International Journal of Refrigeration 2002;25:1093–101.
[27] Filho EPB, Cheng L, Thome JR. Flow boiling characteristics and flow pattern visaulzation of refrigerant/lubricant mixtures. International Journal of Refrigeration 2009;32:185–202.
[28] Wang C, Hafner A, Kuo C, Hsieh W. An overview of the effect of lubricant on the heat transfer performance on conventional refrigerants and natural refrigerant R-744. Renewable and Sustainable Energy Reviews 2012;16:5071–86.
[29] Dang C, Hoshika K, Hihara E. Effect of lubricating oil on the flow and heat-transfer characteristics of supercritical carbon dioxide. International Journal of Refrigeration 2012;35:1410–7.
[30] Gibb P, Randles S, Millington M, Whittaker A. Lubricants for sustainable cooling. In: Proceedings of the 2003 CIBSE/ASHRAE conference, Edinburgh, United Kingdom, 2003.
[31] Wei W, Ding G, Hu H, Wang K. Models of thermodynamic and transport properties of POE VG68 and R410A/POE VG68 mixture. Frontiers of Energy and Power Engineering in China 2008;2(2):227–34.